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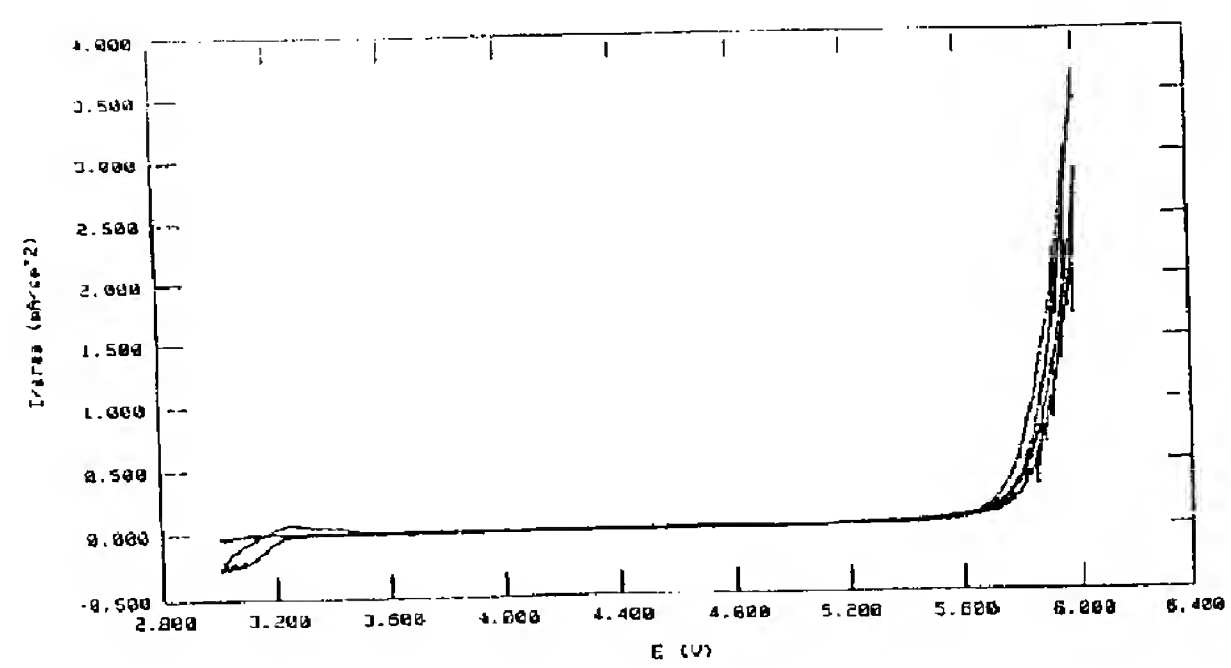
(72)
FRANZ, KLAUS-DIETER (DE).
VAUGHAN, JULIAN (DE).
HEIDER, UDO (DE).
KUHNER, ANDREAS (DE).
OESTEN, RUDIGER (DE).
SCHMIDT, MICHAEL (DE).
WIEDERHOLT, HOLGER (DE).

(74)
FETHERSTONHAUGH & CO.

(54) SELS COMPLEXES POUR UTILISATION DANS DES CELLULES ELECTROCHIMIQUES
(54) COMPLEX SALTS FOR USE IN ELECTROCHEMICAL CELLS

(57)

The invention relates to a process for preparing complex salts and to their use in electrochemical cells.



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(72) HEIDER, UDO, DE
(72) SCHMIDT, MICHAEL, DE
(72) OESTEN, RUDIGER, DE
(72) KUHNER, ANDREAS, DE
(72) FRANZ, KLAUS-DIETER, DE
(72) VAUGHAN, JULIAN, DE
(72) WIEDERHOLT, HOLGER, DE
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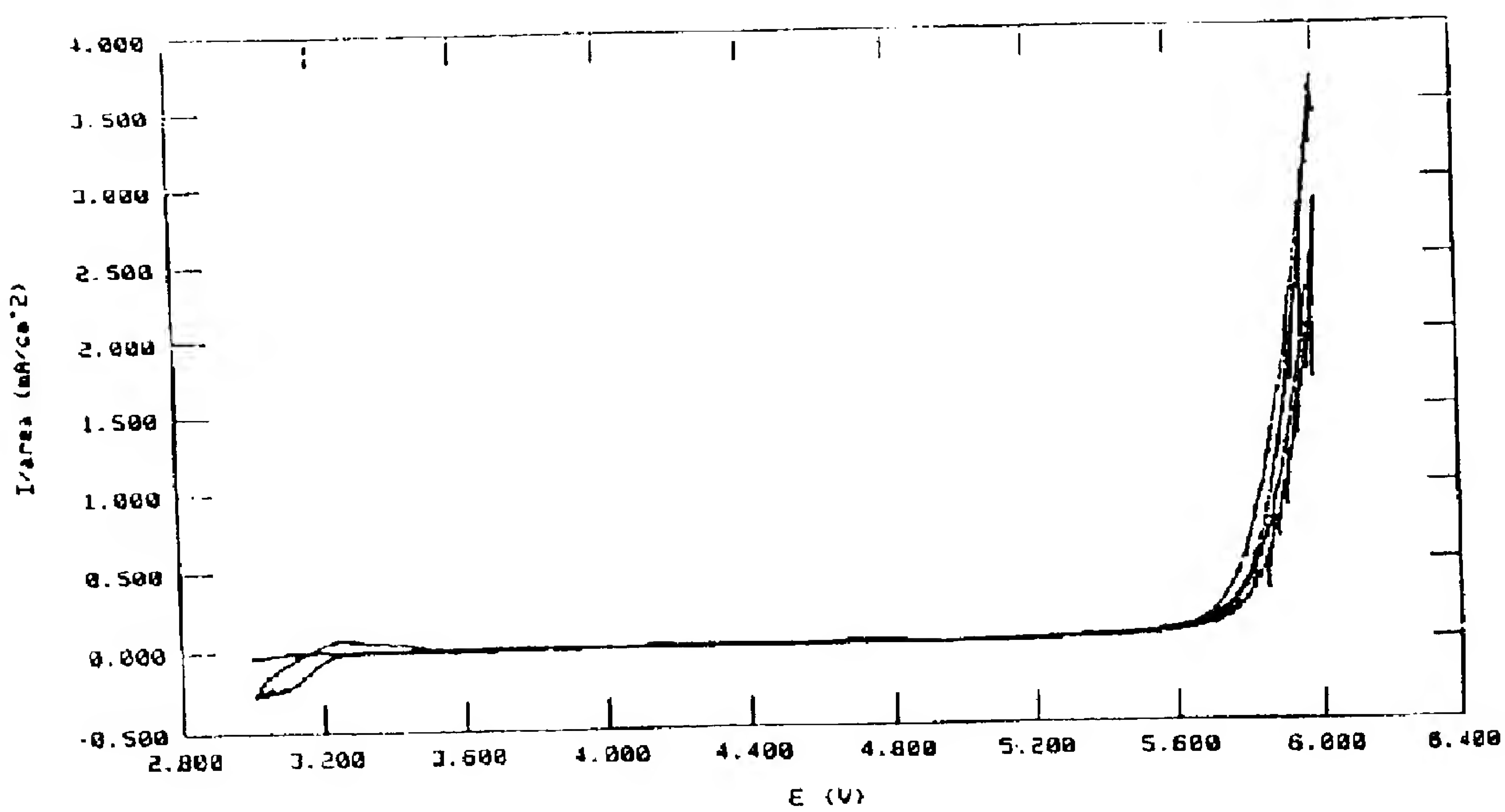
(54) **SELS COMPLEXES POUR UTILISATION DANS DES CELLULES ELECTROCHIMIQUES**

(54) **COMPLEX SALTS FOR USE IN ELECTROCHEMICAL CELLS**



(57) The invention relates to a process for preparing complex salts and to their use in electrochemical cells.

Abstract

The invention relates to a process for preparing complex salts and to their use in electrochemical cells.

Complex salts for use in electrochemical cells

The invention relates to a process for preparing complex salts and to their use in electrochemical cells.

Lithium ion batteries are among the most promising systems for mobile applications. The fields of application extend from high-quality electronic equipment (e.g. mobile telephones, camcorders) to batteries for electrically driven vehicles. Rechargeable lithium batteries have been commercially available since the early 1990s.

These batteries consist of cathode, anode, separator and a nonaqueous electrolyte. As cathode, use is typically made of $Li(MnMe_z)_2O_4$, $Li(COMe_z)O_2$, $Li(CoNi_xMe_z)O_2$ or other lithium intercalation and insertion compounds. Anodes can consist of lithium metal, carbon, graphite, graphitic carbons or other lithium intercalation and insertion compounds or alloy compounds. Electrolytes used are solutions of lithium salts such as $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$ or $LiC(CF_3SO_2)_3$ and mixtures thereof in aprotic solvents.

At present, the $LiPF_6$ used as electrolyte salt in many lithium ion batteries represents a very hydrolysis-sensitive and thermally unstable substance. Contact with atmospheric moisture and/or residual water in the solvents immediately forms hydrofluoric acid HF. Apart from its toxic properties, HF has an adverse effect on the cycling behaviour and thus on the performance of the lithium battery, since metals can be leached from the electrodes.

US 4505997 describes lithium imides and US 5273840 describes lithium methanides. Both salts have a high anodic stability and in organic carbonates form solutions having a high conductivity. Aluminium, the cathodic terminal lead in lithium ion batteries, is not passivated to a sufficient extent, at least by lithium imide. Lithium methanide, on the other hand, is

very costly to prepare and purify. In addition, the electrochemical properties, e.g. oxidation stability and passivation, of aluminium are very dependent on the purity of the methanide.

WO 98 / 07729 therefore describes a new class of electrolyte salts, namely lithium borate complexes. In cycling experiments, these compounds have given particularly good results and have proven to be particularly stable. In combination with other salts, these complexes display a synergistic stabilizing effect against oxidation.

The lithium bis[5-fluoro-2-olatobenzene-sulfonato(2-)O,O']borate(1-) described as electrolyte salt is, owing to its properties, a promising electrolyte salt for use in lithium ion batteries. However, the costly and complicated synthesis of the precursors is problematical.

It is therefore an object of the present invention to provide materials which passivate the cathodic terminal leads and are stable to oxidation processes, and to provide a simple process for preparing these materials.

The object of the invention is achieved by complex salts of the formula

$$M^{x+}[EZ]^{y-}_{x/y} \qquad (I)$$

where:

x,y are 1, 2, 3, 4, 5, 6,

M^{x+} is a metal ion,

E is a Lewis acid selected from the group consisting of

$BR^1R^2R^3$, $AlR^1R^2R^3$, $PR^1R^2R^3R^4R^5$, $AsR^1R^2R^3R^4R^5$, $VR^1R^2R^3R^4R^5$,

R^1 to R^5 are identical or different, may be joined directly to one another by a single or double bond and can each be, either individually or together,

a halogen (F, Cl, Br),

an alkyl or alkoxy radical (C_1 to C_8) which may be partly or fully substituted by F, Cl, Br,

an aromatic ring, which may be bound via oxygen, selected from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or monosubstituted or multiplesubstituted by alkyl (C_1 to C_8) or F, Cl, Br, or

an aromatic heterocyclic ring, which may be bound via oxygen, selected from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or monosubstituted to tetrasubstituted by alkyl (C_1 to C_8) or F, Cl, Br, and

Z is OR^6, NR^6R^7, $CR^6R^7R^8$, OSO_2R^6, $N(SO_2R^6)(SO_2R^7)$, $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$, $OCOR^6$, where

R^6 to R^8 are identical or different, may be joined directly to one another by a single or double bond and are each, either individually or together,

a hydrogen atom or as defined for R^1 to R^5.

These complex salts are particularly suitable as electrolyte salts in electrolytes for electrochemical cells.

It has surprisingly been found that the salts of the invention can passivate transition metal cathodes and terminal leads. The frequently used aluminium terminal leads, in particular, can be protected by passivation against the pit corrosion which occurs in conventional systems.

It has been found that the complex salts of the formula (I) have good electrochemical properties. Thus, for example, good oxidation stability was observed.

It has surprisingly been found that the salts of the invention have greatly improved ion conductivity compared with conventional electrolyte salts.

The complex salts of the formula (I) and their mixtures can be used as electrolyte salts in electrolytes for electrochemical cells. Likewise, they can be used in proportions of from 1 to 99% in combination with other electrolyte salts.

Particularly suitable complex salts of the formula (I) are those in which $M^{x+} = Li^+$ or tetraalkylammonium and $E = BR^1{}_aR^2{}_bF_c$ and $PR^1{}_dR^2{}_eR^3{}_fR^4{}_gF_h$ where a to h = 0, 1, 2, 3, 4 or 5, where a+b+c=3 and d+e+f+g+h=5.

The complex salts of the invention can be used in customary electrolytes. Suitable electrolytes are, for example, those containing electrolyte salts selected from the group consisting of $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$ or $LiC(CF_3SO_2)_3$ and mixtures thereof.

The electrolytes can further comprise organic isocyanates (DE 199 44 603) to reduce the water content. Likewise, organic alkali metal salts (DE 199 10 968) may be present as additives in the electrolytes. Suitable alkali metal salts are alkali metal borates of the formula

$$Li^+B^-(OR^1)_m(OR^2)_p$$

where

m and p are 0, 1, 2, 3 or 4 with m+p=4 and

R^1 and R^2 are identical or different,

may be joined directly to one another by a single or double bond,

are each, either individually or together, an aromatic or aliphatic carboxylic, dicarboxylic or sulfonic acid radical, or

are each, either individually or together, an aromatic ring selected from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or monosubstituted to tetrasubstituted by A or Hal, or

are each, either individually or together, a heterocyclic aromatic ring selected from the group consisting of pyridyl, pyrazyl and bipyridyl, which may be unsubstituted or monosubstituted to trisubstituted by A or Hal, or

are each, either individually or together, an aromatic hydroxy acid selected from the group consisting of aromatic hydroxycarboxylic acids and aromatic hydroxysulfonic acids, which may be unsubstituted or monosubstituted to tetrasubstituted by A or Hal,

and

Hal can be F, Cl or Br

and

A can be alkyl having from 1 to 6 carbon atoms, which may be monohalogenated to trihalogenated.

Likewise suitable are alkali metal alkoxides (DE 9910968) of the formula

$$Li^+ \ OR^-$$

where R

is an aromatic or aliphatic carboxylic, dicarboxylic or sulfonic acid radical, or

is an aromatic ring selected from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or monosubstituted to tetrasubstituted by A or Hal, or

is a heterocyclic aromatic ring selected from the group consisting of pyridyl, pyrazyl and bipyridyl, which may be unsubstituted or monosubstituted to trisubstituted by A or Hal, or

is an aromatic hydroxy acid selected from the group consisting of aromatic hydroxycarboxylic acids and aromatic hydroxysulfonic acids, which may be unsubstituted or monosubstituted to tetrasubstituted by A or Hal,

and

Hal is F, Cl or Br,

and

A is alkyl having from 1 to 6 carbon atoms, which may be monohalogenated to trihalogenated.

Other constituents which may be present are compounds of the formula

$$[([R^1(CR^2R^3)_k]_lA_x)_yKt]^+ \ {}^-N(CF_3)_2$$

where

Kt is N, P, As, Sb, S, Se

A is N, P, P(O), O, S, S(O), SO_2, As, As(O), Sb, Sb(O)

R^1, R^2 and R^3

are identical or different and are each

H, halogen, substituted and/or unsubstituted alkyl C_nH_{2n+1}, substituted and/or unsubstituted alkenyl having 1-18 carbon atoms and one or more double bonds,

substituted and/or unsubstituted alkynyl having 1-18 carbon atoms and one or more triple bonds, substituted and/or unsubstituted cycloalkyl C_mH_{2m-1}, monosubstituted or polysubstituted and/or unsubstituted phenyl, substituted and/or unsubstituted heteroaryl,

A can be included in various positions in R^1, R^2 and/or R^3,

Kt can be included in cyclic or heterocyclic rings,

the groups bound to Kt can be identical or different,

where

n is 1-18,
m is 3-7,
k is 0, 1-6,
l is 1 or 2 when x=1 and 1 when x=0,
x is 0,1,
y is 1-4

(DE 9941566). The process for preparing the compounds is characterized in that an alkali metal salt of the formula

$$D^{+}\ {}^{-}N(CF_3)_2,$$

where D^+ is selected from the group consisting of the alkali metals, is reacted in a polar organic solvent with a salt of the formula

$$[([R^1(CR^2R^3)_k]_lA_x)_yKt]^{+}\ {}^{-}E$$

where

Kt, A, R^1, R^2, R^3, k, l, x and y are as defined above and

^-E is F^-, Cl^-, Br^-, I^-, BF_4^-, ClO_4^-, AsF_6^-, SbF_6^- or PF_6^-.

The compounds of the invention may also be present in electrolytes comprising compounds of the formula

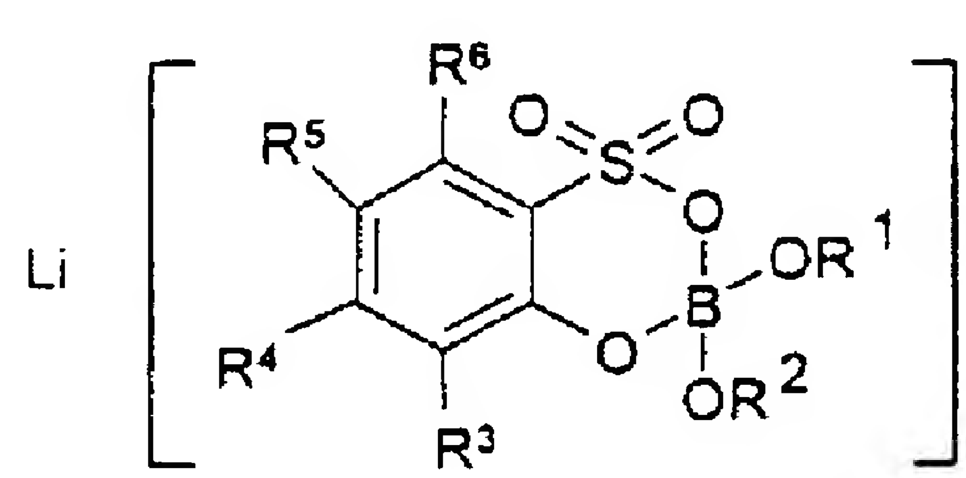
$$X-(CYZ)_m-SO_2N(CR^1R^2R^3)_2$$

where

X is H, F, Cl, C_nF_{2n+1}, C_nF_{2n-1}, $(SO_2)_kN(CR^1R^2R^3)_2$,
Y is H, F, Cl,
Z is H, F, Cl,
R^1, R^2, R^3 are H and/or alkyl, fluoroalkyl, cycloalkyl,
m is 0-9 and when X=H, $m \neq 0$,
n is 1-9 and
k is 0 when m=0 and k=1 when m=1-9,

prepared by reacting partially fluorinated or perfluorinated alkylsulfonyl fluorides with dimethylamine in organic solvents (DE 199 466 73).

Further constituents which may be present are lithium complex salts of the formula



where

R^1 and R^2 are identical or different, may be bound directly to one another by a single or double bond and are each, either individually or together, an aromatic ring selected from the group consisting of phenyl,

naphthyl, anthracenyl and phenanthryl, which may be unsubstituted or monosubstituted to hexasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

or are each, either individually or together, an aromatic heterocyclic ring selected from the group consisting of pyridyl, pyrazyl or pyrimidyl, which may be unsubstituted or monosubstituted to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

or are each, either individually or together, an aromatic ring selected from the group consisting of hydroxybenzenecarboxyl, hydroxynaphthalenecarboxyl, hydroxybenzenesulfonyl and hydroxynaphthalenesulfonyl, which may be unsubstituted or monosubstituted to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

R^3-R^6 may each, either individually or in pairs, possibly joined directly to one another by a single or double bond, have the following meanings:

1. alkyl (C_1 to C_6), alkyloxy (C_1 to C_6) or halogen (F, Cl, Br)

2. an aromatic ring selected from the groups consisting of

phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or monosubstituted to hexasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

pyridyl, pyrazyl and primidyl, which may be unsubstituted or monosubstituted to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl, Br),

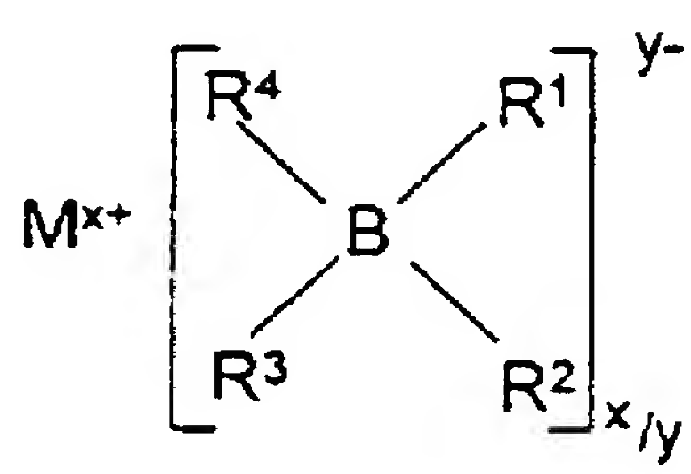
which are prepared by the following method (DE 199 32 317):

a) 3-, 4-, 5-, 6-substituted phenol is admixed in a suitable solvent with chlorosulfonic acid,

b) the intermediate from a) is reacted with chlorotrimethylsilane, filtered and fractionally distilled,

c) the intermediate from b) is reacted in a suitable solvent with lithium tetramethoxyborate (1-) and the end product is isolated therefrom, may also be present in the electrolyte.

Borate salts (DE 199 59 722) of the formula



where:

M is a metal ion or tetraalkylammonium ion,

x,y are 1, 2, 3, 4, 5 or 6 and

R^1 to R^4 are identical or different and are alkoxy or carboxy radicals (C_1-C_8) which may be bound directly to one another by a single or double bond, may also be present. These borate salts are prepared by reacting lithium tetraalkoxyborate or a 1:1 mixture of lithium alkoxide and a boric ester in an aprotic solvent with a suitable hydroxyl or carboxyl compound in a ratio of 2:1 or 4:1.

Additives such as silane compounds of the formula

$SiR^1R^2R^3R^4$

where R^1 to R^4 are H
$C_yF_{2y+1-z}H_z$
$OC_yF_{2y+1-z}H_z$
$OC(O)C_yF_{2y+1-z}H_z$
$OSO_2C_yF_{2y+1-z}H_z$

and $1 \leq x < 6$
$1 \leq y \leq 8$ and
$0 \leq z \leq 2y + 1$

and

R^1-R^4 are identical or different and

are each an aromatic ring selected from the group consisting of phenyl and naphthyl, which may be unsubstituted or monosubstituted or polysubstituted by F, $C_yF_{2y+1-z}H_z$ or $OC_yF_{2y+1-z}H_z$, $OC(O)C_yF_{2y+1-z}H_z$, $OSO_2C_yF_{2y+1-z}H_z$, $N(C_nF_{2n+1-z}H_z)_2$, or

are each a heterocyclic aromatic ring selected from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may each be monosubstituted or polysubstituted by F, $C_yF_{2y+1-z}H_z$ or $OC_yF_{2y+1-z}H_z$, $OC(O)C_yF_{2y+1-z}H_z$, $OSO_2C_yF_{2y+1-z}H_z$, $N(C_nF_{2n+1-z}H_z)_2$ (DE 100 276 26), may also be present.

The compounds of the invention can also be used in electrolytes comprising lithium fluoroalkylphosphates of the following formula,

$$Li^+[PF_x(C_yF_{2y+1-z}H_2)_{6-x}]^-$$

where
$1 \leq x \leq 5$,
$3 \leq y \leq 8$,
$0 \leq z \leq 2y + 1$,

and the ligands $(C_yF_{2y+1-z}H_z)$ may be identical or different, with the exception of the compounds of the formula,

$$Li^+[PF_a(CH_bF_c(CF_3)_d)_e]^-$$

in which a is an integer from 2 to 5, b = 0 or 1, c = 0 or 1, d = 2 and

e is an integer from 1 to 4, with the provisos that b and c are not simultaneously 0 and the sum of a + e is 6 and the ligands $(CH_bF_c(CF_3)_d)$ may be identical or different (DE 100 089 55). The process for preparing lithium fluoroalkylphosphates is characterized in that at least one compound of the formula

$$H_mP(C_nH_{2n+1})_{3-m}\ \text{(III)},$$
$$OP(C_nH_{2n+1})_3\ \text{(IV)},$$
$$Cl_mP(C_nH_{2n+1})_{3-m}\ \text{(V)},$$
$$F_mP(C_nH_{2n+1})_{3-m}\ \text{(VI)},$$
$$Cl_oP(C_nH_{2n+1})_{5-o}\ \text{(VII)},$$
$$F_oP(C_nH_{2n+1})_{5-o}\ \text{(VIII)},$$

in each of which

$0 < m < 2$, $3 < n < 8$ and $0 < o < 4$,

is fluorinated by electrolysis in hydrogen fluoride, the resulting mixture of fluorination products is fractionated by extraction, phase separation and/or distillation and the fluorinated alkylphosphorane obtained in this way is reacted in an aprotic solvent or solvent mixture with lithium fluoride in the absence of moisture, and the resulting salt is purified and isolated by customary methods.

The compounds of the invention can also be used in electrolytes comprising salts of the formula

$$Li[P(OR^1)_a(OR^2)_b(OR^3)_c(OR^4)_dF_e]$$

where $0 < a+b+c+d \leq 5$ and $a+b+c+d+e=6$, and R^1 to R^4 are, independently of one another, alkyl, aryl or

heteroaryl radicals, where at least two of R^1 to R^4 may be joined directly to one another by a single or double bond (DE 100 16801). The compounds are prepared by reacting phosphorus(V) compounds of the formula

$$P(OR^1)_a(OR^2)_b(OR^3)_c(OR^4)_dF_e$$

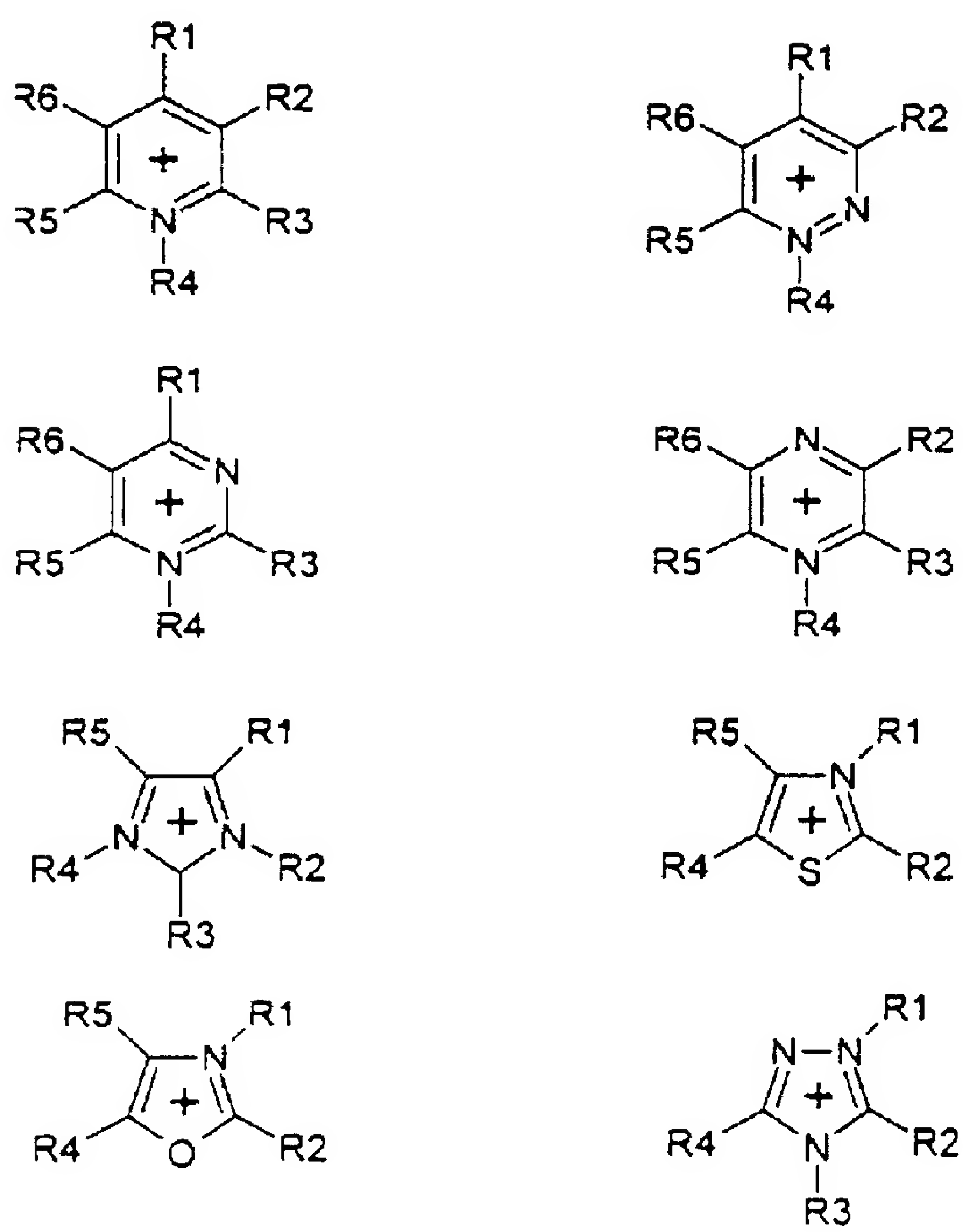
where $0 < a+b+c+d \leq 5$ and $a+b+c+d+e=5$, and R^1 to R^4 are as defined above, with lithium fluoride in the presence of an organic solvent.

It is also possible for ionic liquids of the formula

$$K^+A^-$$

where

K^+ is a cation selected from the group consisting of



where R^1 to R^5 are identical or different, may be joined directly to one another by a single or double bond and are each, either individually or together:

- H,

- halogen,

- an alkyl radical (C_1 to C_8) which may be partially or fully substituted by further groups, preferably F, Cl, $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$, $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$,

A^- is an anion selected from the group consisting of

$$[B(OR^1)_n(OR^2)_m(OR^3)_o(OR^4)_p]^-$$

where $0\leq n, m, o, p\leq 4$ and

$m+n+o+p=4$

where R^1 to R^4 are different or identical in pairs, may be joined directly to one another by a single or double bond and are each, either individually or together,

an aromatic ring selected from the group consisting of phenyl, naphthyl, anthracenyl or phenanthrenyl, which may be unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$ or halogen (F, Cl, Br),

an aromatic heterocyclic ring selected from the group consisting of pyridyl, pyrazyl or pyrimidyl, which may be unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$ or halogen (F, Cl, Br), or

an alkyl radical (C_1 to C_8) which may be partially or fully substituted by further groups, preferably F, Cl, $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$, $C_nF_{-(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$,

or OR^1 to OR^4 are each, either individually or together,

an aromatic or aliphatic carboxyl, dicarboxyl, oxysulfonyl or oxycarboxyl radical which may be partially or fully substituted by further groups, preferably F, Cl, $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$, $C_nF_{-(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$ (DE 100 265 65), to be present in the electrolyte. Ionic liquids K^+A^- where K^+ is as defined above and

A^- is an anion selected from the group consisting of

$$\left[PF_x(C_yF_{2y+1-z}H_z)_{6-x}\right]^-$$

where $1 \leq x < 6$,
$1 \leq y \leq 8$ and
$0 \leq z \leq 2y + 1$,

can also be present (DE 100 279 95).

The compounds of the invention can be used in electrolytes for electrochemical cells which comprise anode material consisting of coated metal nuclei selected from the group consisting of Sb, Bi, Cd, In, Pb, Ga and tin or their alloys (DE 100 16 024). The process for preparing this anode material is characterized in that

a) a suspension or a sol of the metal or alloy nucleus in urotropin is prepared,
b) the suspension is emulsified with C_5-C_{12}-hydrocarbons,
c) the emulsion is precipitated onto the metal or alloy nuclei and

d) the metal hydroxides or oxyhydroxides are converted into the corresponding oxide by heat treatment of the system.

The compounds of the invention can also be used in electrolytes for electrochemical cells having cathodes of customary lithium intercalation and insertion compounds or else comprising cathode materials consisting of lithium mixed oxide particles which are coated with one or more metal oxides (DE 199 22 522) by suspending the particles in an organic solvent, admixing the suspension with a solution of a hydrolysable metal compound and a hydrolysis solution and then filtering off, drying and, if appropriate, calcining the coated particles. They can also consist of lithium mixed oxide particles which are coated with one or more polymers (DE 199 46 066), obtained by a process in which the particles are suspended in a solvent and the coated particles are subsequently filtered off, dried and, if appropriate, calcined. Likewise, the compounds of the invention can be used in systems having cathodes consisting of lithium mixed oxide particles which are coated with one or more layers of alkali metal compounds and metal oxides (DE 100 14 884). The process for preparing these materials is characterized in that the particles are suspended in an organic solvent, an alkali metal salt compound suspended in an organic solvent is added, metal oxides dissolved in an organic solvent are added, the suspension is admixed with a hydrolysis solution and the coated particles are subsequently filtered off, dried and calcined. Likewise, the compounds of the invention can be used in systems having cathodes comprising anode materials with doped tin oxide (DE 100 257 61). This anode material is prepared by

a) admixing a tin chloride solution with urea,

b) admixing the solution with urotropin and a suitable dopant,

c) emulsifying the resulting sol in petroleum ether,

d) washing the gel obtained and taking off the solvent and

e) drying and heat-treating the gel.

The compounds of the invention can likewise be used in systems having cathodes comprising anode materials with reduced tin oxide (DE 100 257 62). This anode material is prepared by

a) admixing a tin chloride solution with urea,

b) admixing the solution with urotropin,

c) emulsifying the resulting sol in petroleum ether,

d) washing the gel obtained and taking off the solvent,

e) drying and heat-treating the gel and

f) exposing the SnO_2 obtained to a reducing gas stream in a furnace into which gas can be introduced.

The complex salts of the invention are thus particularly suitable as electrolyte salts for lithium ion batteries and supercapacitors.

In the following, a general example of the invention will be described in more detail.

Use is made of Lewis acid-solvent adducts, preferably selected from the group consisting of $BR^1R^2R^3$, $AlR^1R^2R^3$, $PR^1R^2R^3R^4R^5$, $AsR^1R^2R^3R^4R^5$, $VR^1R^2R^3R^4R^5$,

where

R^1 to R^5 are identical or different, may be joined directly to one another by a single or double bond and are each, either individually or together,

a halogen (F, Cl, Br),

an alkyl or alkoxy radical (C_1 to C_8) which may be partially or fully substituted by halogen (F, Cl, Br),

an aromatic ring, which may be bound via oxygen, selected from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or monosubstituted or multiplesubstituted by alkyl (C_1 to C_8) or F, Cl, Br,

an aromatic heterocyclic ring, which may be bound via oxygen, selected from the group consisting of pyridyl, pyrazyl or pyrimidyl, which may be unsubstituted or monosubstituted to tetrasubstituted by alkyl (C_1 to C_8) or F, Cl, Br.

These adducts are dissolved in suitable battery solvents, preferably selected from the group consisting of dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, ethyl methyl carbonate, methyl propyl carbonate, γ-butyrolactone, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate, dimethyl sulfoxide, dioxolane, sulfolane, acetonitrile, acrylonitrile, tetrahydrofuran, 2-methyltetrahydrofuran and mixtures thereof.

Addition of metal salts in which the anion is selected from the group consisting of

OR^6, NR^6R^7 or $CR^6R^7R^8$,

OSO_2R^6, $N(SO_2R^6)(SO_2R^7)$, $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$ or $OCOR^6$, where

R^6 to R^8 are identical or different, may be joined directly to one another by a single or double bond and are each, either individually or together,

a hydrogen atom or as defined for R^1 to R^5, gives compounds of the formula (I).

Particular preference is given to preparing compounds of the formula (I) where $M^{x+} = Li^+$ or a tetraalkylammonium ion and $E=BR^1_aR^2_bF_c$ and $PR^1_dR^2_eR^3_fR^4_gF_h$, where a to h = 0, 1, 2, 3, 4 or 5, where a+b+c=3 and

d+e+f+g+h=5, by reacting a corresponding boron or phosphorus Lewis acid-solvent adduct with a lithium or tetraalkylammonium-imide, -methanide or -triflate.

The following examples are intended to illustrate the invention without restricting it.

Examples

Example 1

Preparation of the complex salt $Li[BF_3 \cdot N(SO_2CF_3)_2]$

Diethyl carbonate is treated at room temperature with boron trifluoride gas for 20 minutes. Here, the reaction temperature is maintained at 40°C by external cooling. On cooling, a colourless, crystalline BF_3 · diethyl carbonate precipitates. The solid is filtered off under protective gas and dried under reduced pressure at room temperature.

A mixture of 29.7 g of ethylene carbonate and 26.22 g of diethyl carbonate is placed in a PTFE reaction vessel. While cooling, 5.5 g (0.03 mol) of BF_3 · diethyl carbonate and 8.5 g (0.03 mol) of lithium imide $Li[N(SO_2CF_3)_2]$ are added. The solution obtained is used directly as battery electrolyte comprising $Li[BF_3 \cdot N(SO_2CF_3)_2]$ as electrolyte salt.

Concentration of the electrolyte salt: 0.5 $mol/kg_{solvent}$

^{19}F-NMR (282 MHz, CD_3CN)

ppm: -151 s (3F), 3 B-F

-80 s (6 F), 2 SO_2C-F_3

Example 2

Preparation of the complex salt $Li[BF_3 \cdot SO_3CF_3]$

Diethyl carbonate is treated at room temperature with boron trifluoride gas for 20 minutes. Here, the reaction temperature is maintained at 40°C by external cooling. On cooling, a colourless, crystalline

BF_3 · diethyl carbonate precipitates. The solid is filtered off under protective gas and dried under reduced pressure at room temperature.

A mixture of 31.50 g of ethylene carbonate and 27.82 g of diethyl carbonate is placed in a PTFE reaction vessel. While cooling, 8.80 g (0.03 mol) of BF_3 · diethyl carbonate and 4.80 g (0.03 mol) of lithium triflate $Li[SO_3CF_3]$ are added. The solution obtained is used directly as battery electrolyte comprising $Li[BF_3 \cdot SO_3CF_3]$ as electrolyte salt.

Concentration of the electrolyte salt: 0.5 mol/$kg_{solvent}$

^{19}F-NMR (282 MHz, CD_3CN)
ppm: -149 s (3F), 3 B-F
-79 s (3F), 1 SO_3C-F_3

Example 3

Electrochemical stability of the electrolytes

A plurality of cyclovoltammmograms were in each case recorded in succession in a measurement cell having a platinum electrode, a lithium counterelectrode and a lithium reference electrode. For this purpose, the potential was firstly increased from the rest potential to 6 V against Li/Li^+ at a rate of 20 mV/s and subsequently brought back to the rest potential. As electrolytes, the solutions indicated in Examples 1 and 2 were used.

The characteristic curve shown in Figures 1 and 2 is obtained. The electrolytes are thus suitable for use in lithium ion batteries having a transition metal cathode.

Example 4

Ion conductivity of the electrolytes

The ion conductivity of the electrolyte salts was measured in a solvent mixture of EC/DEC (1:1) at a concentration of 0.5 mol/kg and a temperature of 25°C.

Electrolyte salt	Conductivity [mS/cm]
$Li[BF_3 \cdot N(SO_2CF_3)_2]$	4.8
$Li[N(SO_2CF_3)_2]$	4.5
$Li[BF_3 \cdot SO_3CF_3]$	3.7
$Li[SO_3CF_3]$	1.9

The sometimes greatly improved conductivities of the complex salts compared with the comparison compounds indicate that they are good electrolyte salts for electrochemical cells.

Example 5

Passivation of aluminium

A plurality of cyclovoltammmograms were in each case recorded in succession in a measurement cell having an aluminium electrode, a lithium counter-electrode and a lithium reference electrode. For this purpose, the potential was firstly increased from the rest potential to 5 V against Li/Li^+ at a rate of 20 mV/s and subsequently brought back to the rest potential. As electrolytes, the solutions indicated in Examples 1 and 2 were used.

The characteristic curve shown in Figure 4 ($Li[BF_3\ N(SO_2CF_3)_2]$) and Figure 5 ($Li[BF_3\ SO_3CF_3]$) is obtained. The decrease in the current with increasing number of cycles indicates passivation of the aluminium. After the experiment, no corrosion of the aluminium can be seen. The electrolyte is thus suitable for use in lithium ion batteries having a transition metal cathode.

Comparative Example 1

Corrosion of aluminium

A plurality of cyclovoltammmograms were in each case recorded in succession in a measurement cell having an aluminium electrode, a lithium counter-electrode and a lithium reference electrode. For this purpose, the potential was firstly increased from the rest potential to 5 V against Li/Li^+ at a rate of 20 mV/s and subsequently brought back to the rest potential. Solutions of lithium imide $Li[N(SO_2CF_3)_2]$ or lithium triflate $Li[SO_3CF_3]$ in EC/DEC 1:1 were used as electrolyte.

Both electrodes display the same, characteristic current-voltage curve. The increase in current with increasing number of cycles indicates corrosion of the aluminium. After the experiments, clear signs of corrosion (pit corrosion) can be seen. Figure 3 shows, by way of example, the curve in the lithium imide electrolyte. The electrolytes are thus not suitable for use in lithium ion batteries having a transition metal cathode and aluminium terminal leads.

Claims

1. Complex salts of the formula

$$M^{x+}[EZ]^{y-}_{x/y} \qquad (I)$$

where:

x,y are 1, 2, 3, 4, 5, 6,
M^{x+} is a metal ion,
E is a Lewis acid selected from the group consisting of

$BR^1R^2R^3$, $AIR^1R^2R^3$, $PR^1R^2R^3R^4R^5$, $AsR^1R^2R^3R^4R^5$, $VR^1R^2R^3R^4R^5$,

R^1 to R^5 are identical or different, may be joined directly to one another by a single or double bond and can each be, either individually or together,

a halogen (F, Cl, Br),

an alkyl or alkoxy radical (C_1 to C_8) which may be partly or fully substituted by F, Cl, Br,

an aromatic ring, which may be bound via oxygen, selected from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or monosubstituted or multiplesubstituted by alkyl (C_1 to C_8) or F, Cl, Br, or

an aromatic heterocyclic ring, which may be bound via oxygen, selected from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or monosubstituted to tetrasubstituted by alkyl (C_1 to C_8) or F, Cl, Br, and

Z is OR^6, NR^6R^7, $CR^6R^7R^8$, OSO_2R^6, $N(SO_2R^6)(SO_2R^7)$, $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$, $OCOR^6$, where

R^6 to R^8 are identical or different, may be joined directly to one another by a single or double bond and are each, either individually or together,

a hydrogen atom or as defined for R^1 to R^5.

2. Complex salts according to Claim 1, characterized in that M^{x+} is Li^+ or tetraalkylammonium and E is $BR^1{}_aR^2{}_bF_c$ and $PR^1{}_dR^2{}_eR^3{}_fR^4{}_gF_h$ where a to h = 0, 1, 2, 3, 4 or 5, where a+b+c=3 and d+e+f+g+h=5.

3. Process for preparing compounds of the formula (I) in which M^{x+} = Li^+ or a tetraalkylammonium ion and E = $BR^1{}_aR^2{}_bF_c$ and $PR^1{}_dR^2{}_eR^3{}_fR^4{}_gF_h$ where a to h = 0, 1, 2, 3, 4 or 5, where a+b+c=3 and d+e+f+g+h=5, by reacting a corresponding boron or phosphorus Lewis acid-solvent adduct with a lithium or tetraalkylammonium-imide, -methanide or -triflate.

4. Use of compounds according to Claim 1 and their mixtures as electrolyte salt in electrolytes for electrochemical cells.

5. Use of compounds according to Claim 1 in mixtures with other electrolyte salts in electrolytes for electrochemical cells.

6. Use of compounds according to Claim 1 and their mixtures or in mixtures with other electrolyte salts in electrolytes for batteries and supercapacitors.

Fetherstonhaugh & Co.
Ottawa, Canada
Patent Agents

Fig. 1

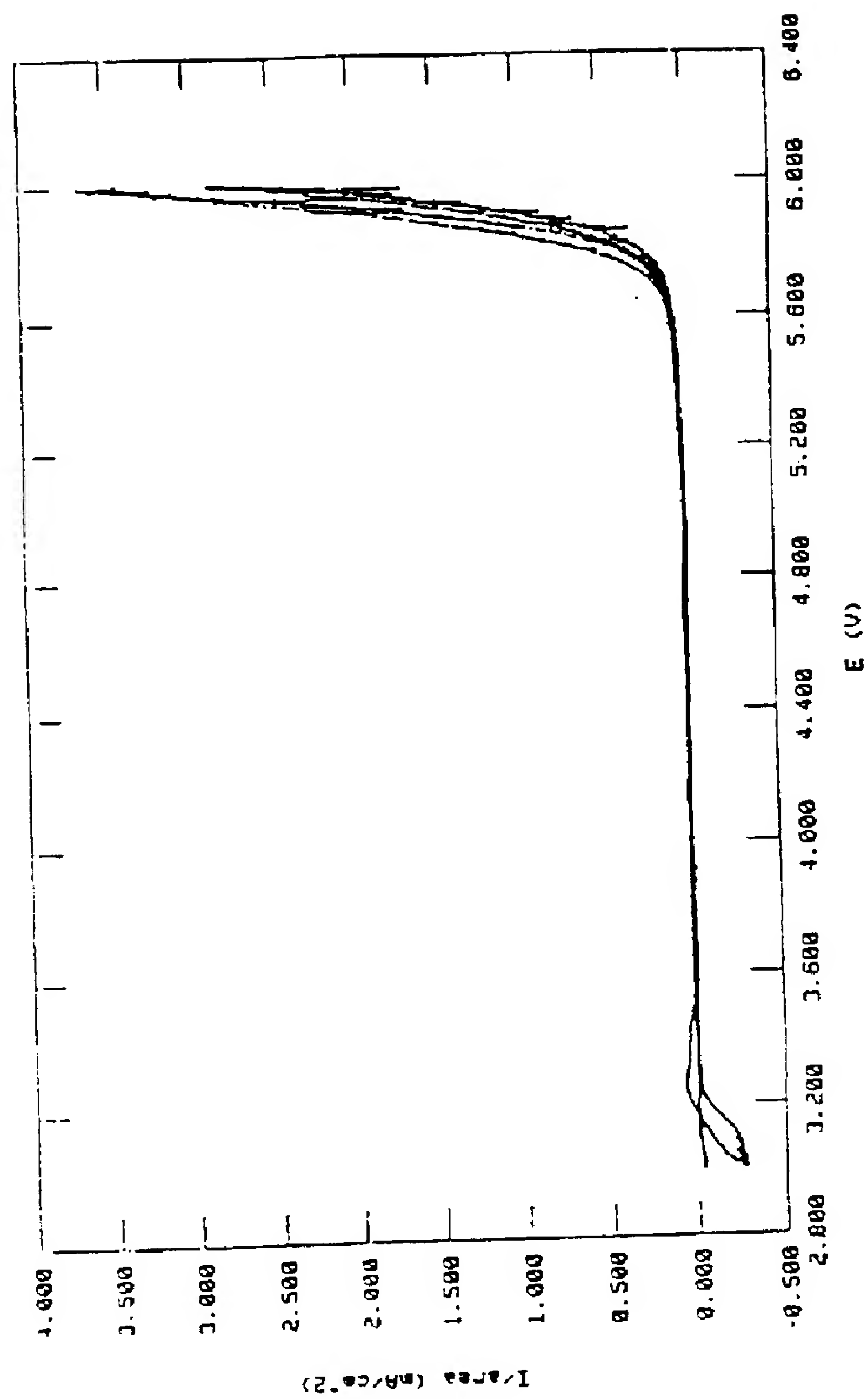

E (V)
I/area (mA/cm^2)
2.800
3.200
3.600
4.000
4.400
4.800
5.200
5.600
6.000
6.400
-0.500
0.000
0.500
1.000
1.500
2.000
2.500
3.000
3.500
4.000

Fig. 2

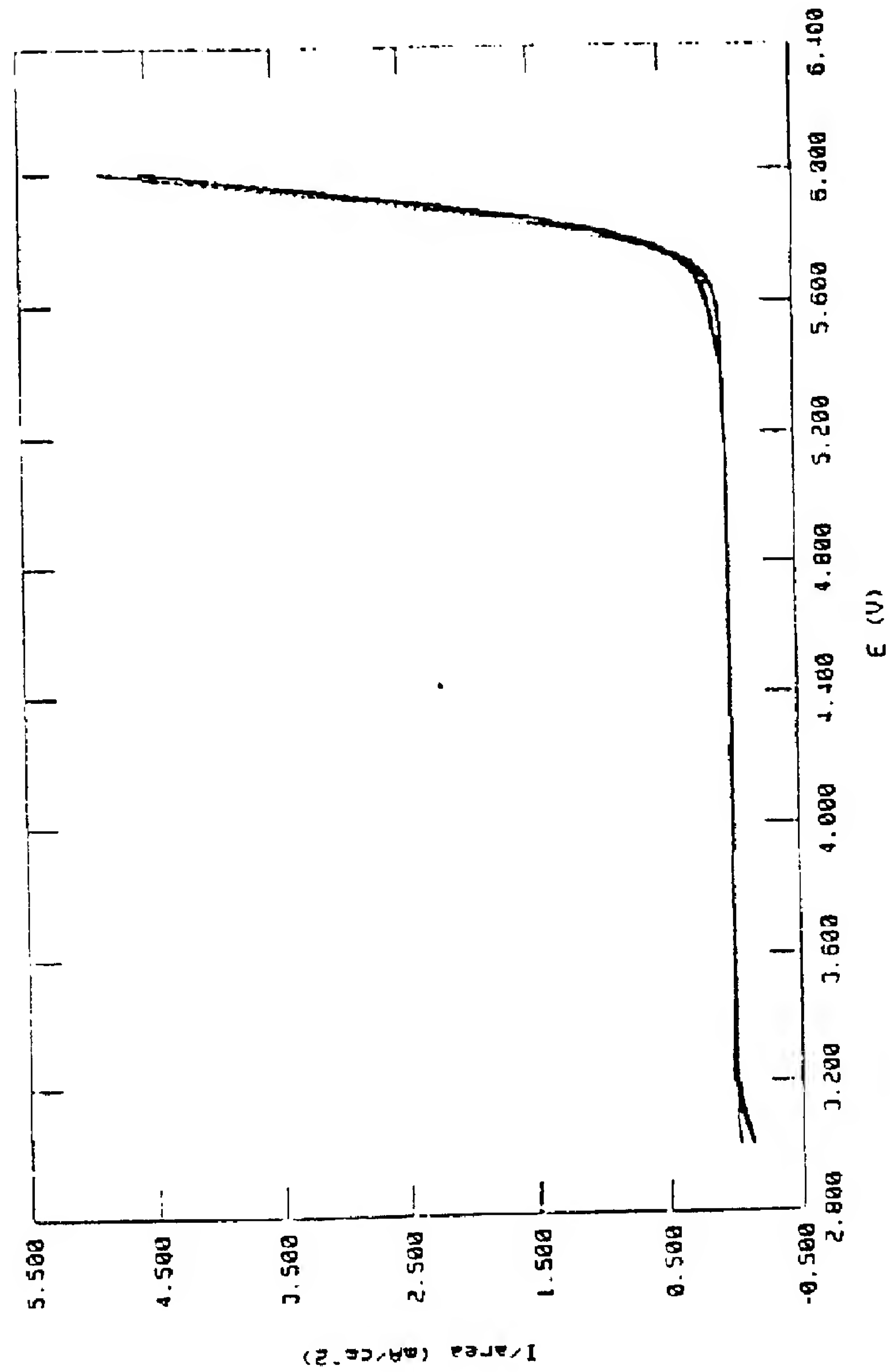

E (V)
I/area (mA/cm^2)
2.800
3.200
3.600
4.000
4.400
4.800
5.200
5.600
6.000
6.400
-0.500
0.500
1.500
2.500
3.500
4.500
5.500

Fig. 3

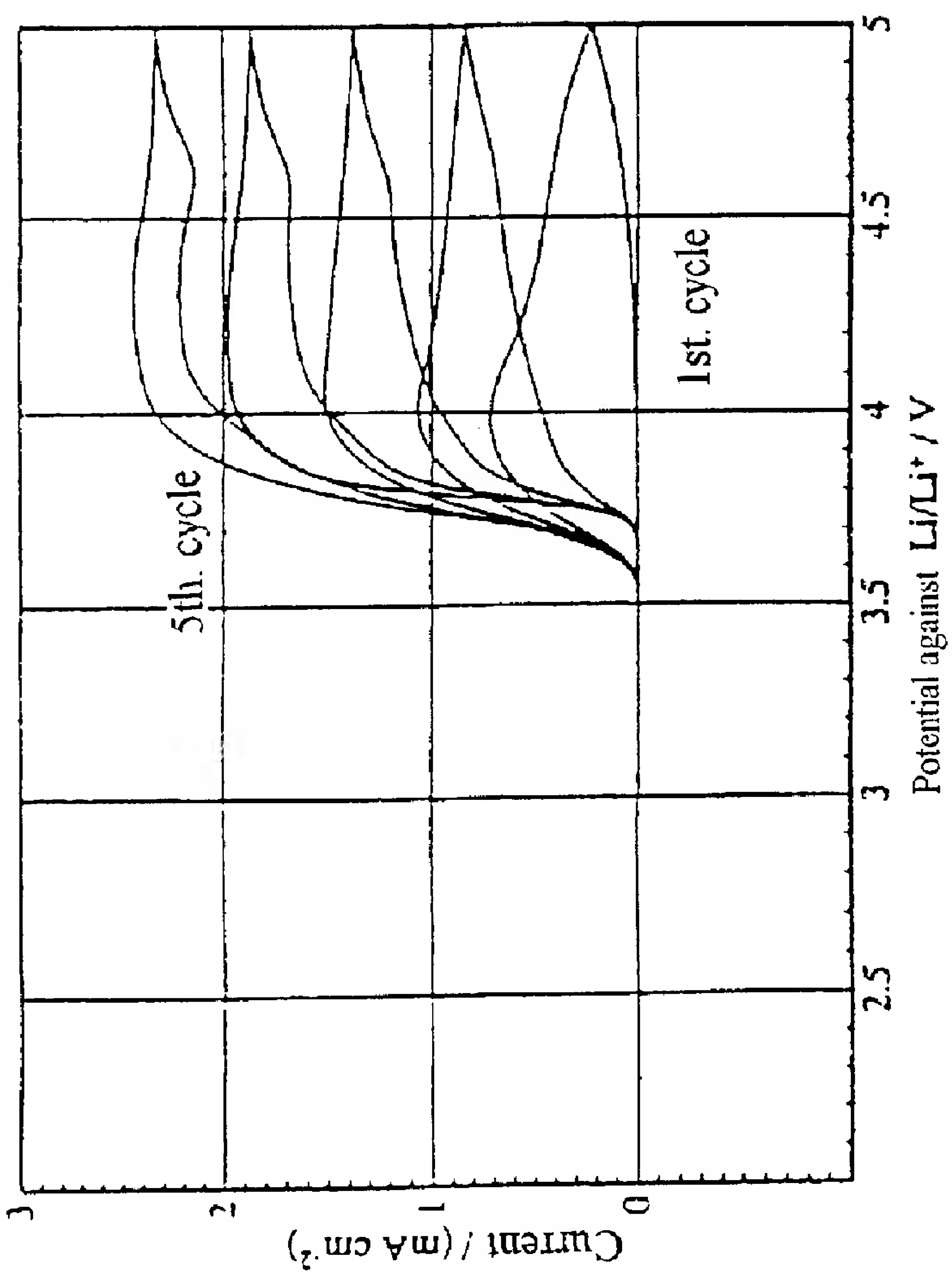

5th. cycle
1st. cycle
Current / (mA cm-2)
Potential against Li/Li+ / V
0
1
2
3
2.5
3
3.5
4
4.5
5

Fig. 4

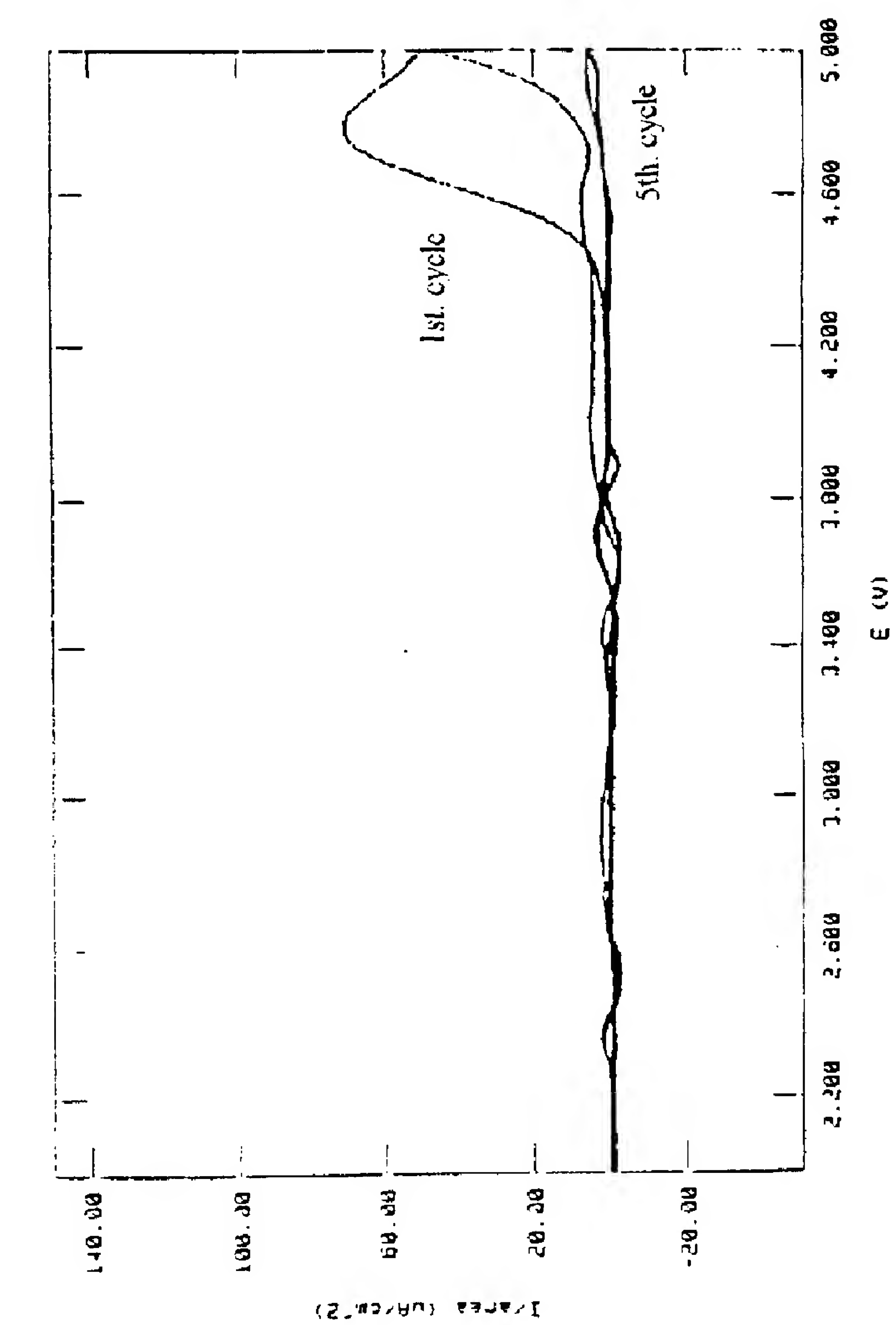
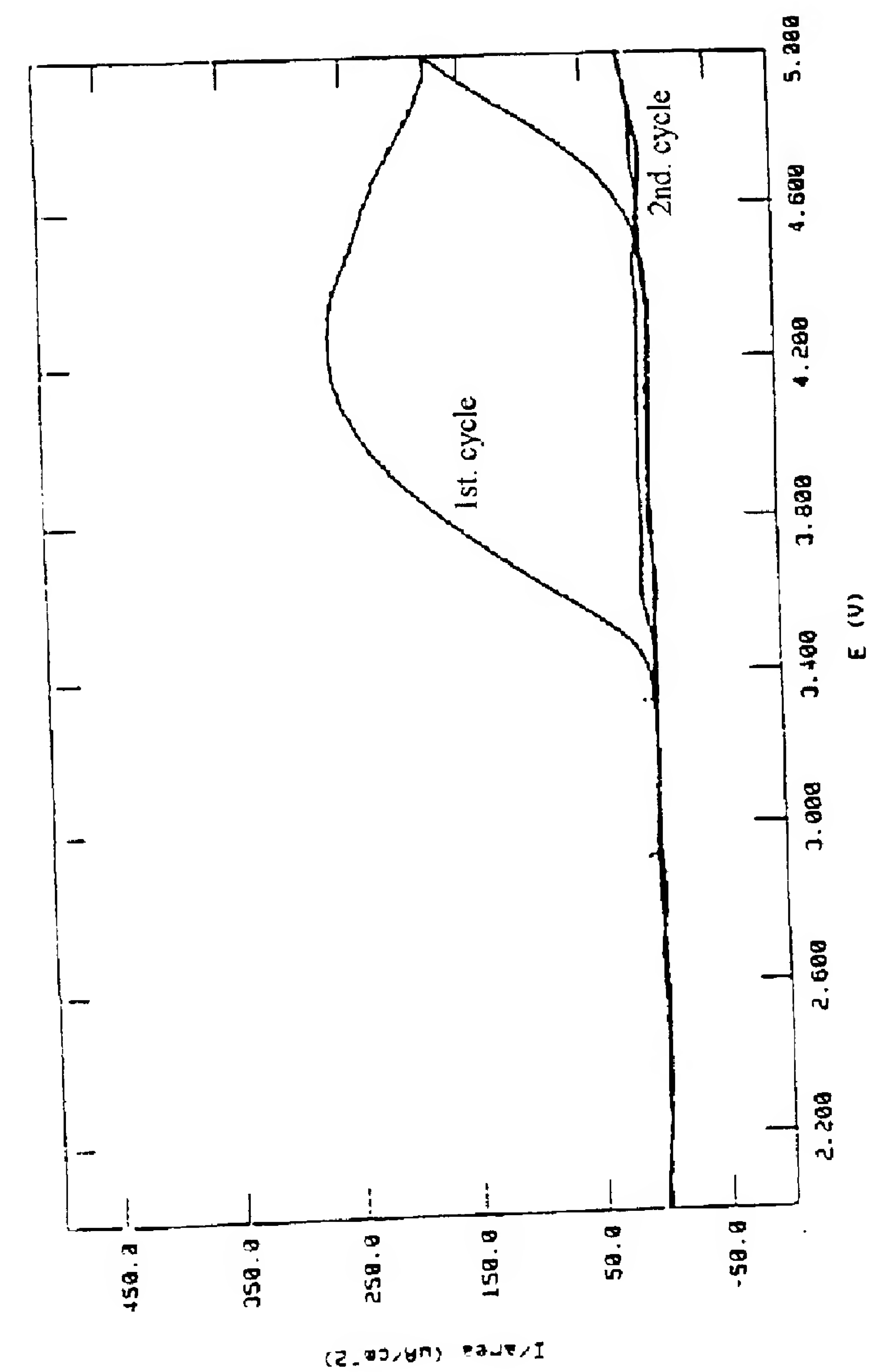

1st. cycle
5th. cycle
E (V)
I/area (uA/cm^2)
140.00
100.00
60.00
20.00
-20.00
2.200
2.600
3.000
3.400
3.800
4.200
4.600
5.000

Fig. 5


1st. cycle
2nd. cycle
E (V)
2.200
2.600
3.000
3.400
3.800
4.200
4.600
5.000
I/area (uA/cm^2)
450.0
350.0
250.0
150.0
50.0
-50.0